



Arsenic in Rice Agro-Ecosystem: Solutions for Safe and Sustainable Rice Production

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Arsenic (As) is a toxic metalloid classified as group 1 carcinogen. The presence of As in high concentrations in paddy soil and irrigation water results into high As accumulation in rice grains posing a threat to the health of millions of people worldwide. The main reason for As contamination is the biogeochemical weathering of rocks and the release of bound As into groundwater. Human interventions through intensive agricultural practices and excessive groundwater consumption have contributed greatly to the prevailing As contamination. The flooded cultivation practice of rice favors the accumulation of As in rice grains. The formation of iron (Fe) plaque on paddy root surfaces, changes in the level of Fe and manganese (Mn) hydro(oxides), soil organic matter, soil pH, soil redox potential, and microbial activities under flooding conditions influence concentrations of various As species in the water-soil-paddy agroecosystem and favor the predominance of highly mobile arsenite [As(III)]. Once inside the rice plant, the concentration of As is regulated by arsenate reduction, arsenite efflux, root-to-shoot translocation, and vacuolar sequestration of As. The detailed understanding gained about the factors affecting As dynamics in soil and transport in rice plants may be helpful in developing feasible methods for sustainable cultivation of rice plants with low grain As. There is also need to ensure high production yields as well as grain quality to achieve the goals of sustainable development. This article discusses the aspects of As in the water-soil-paddy agroecosystem and presents suitable strategies to reduce the As load in rice grains.

Keywords: aerobic irrigation, arsenic, iron plaque, rice, sprinkler irrigation

INTRODUCTION

Arsenic (As) is an important geogenic contaminant found ubiquitously in the earth. Arsenic contamination of food and water is considered a global menace, threatening the health of \sim 150 million people worldwide (Majumder and Banik, 2019; Shikawa et al., 2019). The major sources of As exposure to humans include water and food items, especially rice. Arsenic exposure is associated with various chronic and acute health problems to humans that include skin lesions, cardiovascular diseases, diabetes, cancer, and so on (Shikawa et al., 2019). The As bound to Fe hydroxides, oxyhydroxides, and oxides has released in the recent past into groundwater through biogeochemical processes (Majumdar and Bose, 2017) and has resulted in widespread

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As contamination in India and Bangladesh (Raessler, 2018). In the Indian context, the region of As contamination, the Gangetic basin, is also renowned for extensive rice cultivation. The most common rice cultivation practice is flooded irrigation, and in absence of rains, groundwater is used. The repeated use of Asladen groundwater has resulted in As build-up in soil through the years (Upadhyay et al., 2019a). Rice can accumulate As in several-fold higher levels than other cereal crops such as wheat and maize (Williams et al., 2007; Shikawa et al., 2019; Upadhyay et al., 2019a). In reducing conditions of flooded paddy fields, arsenite [As(III)] is present in higher concentrations than arsenate [As(V)] (Meharg and Jardine, 2003). Other As forms also exist, which include organic methylated forms such as methylarsenate [MAs(V)], methylarsenite [MAs(III)], dimethylarsenate [DMAs(V)], dimethylarsenite [DMAs(III)], trimethylarsine [TMAs(III)] trimethylarsineoxide [TMAs(V)O] (Upadhyay et al., 2019b), and thio-arsenates (Kerl et al., 2019). Various factors such as pH, redox potential, dissolved organic carbon, organic matter, and biotic factors play a significant role in determining the bioavailability of various As species in the soil system (Majumdar et al., 2018). Rice roots release oxygen, which causes oxidation of Fe^{2+} to Fe^{3+} and leads to the formation of iron plaque at the rice root surface. The adsorption of As by iron plaque increases the rhizospheric concentration of As around rice roots (Zhao et al., 2010; Hu et al., 2019). Further, As itself affects iron plaque formation, and there are also varietal influences on iron plaque formation due to differences in root oxidation abilities of different varieties (Lee et al., 2013).

The transporters involved in the uptake of As and translocation from root to shoot and grains play a crucial role in As build-up in plants. The extensive research conducted to date has resulted in identification of several transporters (Awasthi et al., 2017), such as aquaglyceroporins for As(III) and organic As species (Ma et al., 2008; Mosa et al., 2012; Lindsay and Maathuis, 2017), phosphate transporters for As(V) (Catarecha et al., 2007; Wang et al., 2016), ATP-binding cassette-type transporters for As-thiol complexes (Song et al., 2010, 2014), and inositol transporters and peptide transporter for grain/seed As accumulation (Duan et al., 2015). Furthermore, metabolites and genes/proteins involved in internal As metabolism in plants have also been discovered. To this end, the role of enzymes involved in As(V) to As(III) reduction is important, and these include high As content 1;1/1;2/4 (HAC1;1/1;2/4) (Shi et al., 2016; Xu et al., 2017) in rice. Significant progress has been made in understanding holistic biochemical, proteomic, and transcriptomic changes in response to As stress in plants (Chakrabarty et al., 2009; Srivastava et al., 2015). However, the development of low-As accumulating rice varieties through the use of genes/proteins by employing molecular techniques is not yet feasible. The As accumulation in rice grains varies significantly in different rice varieties (Norton et al., 2009). In West Bengal, India, the As concentration in five rice varieties (Satabdi, Gosai, Banskathi, Kunti, Ranjit) was recorded to range between 0.29 and 0.95 mg kg⁻¹ (Upadhyay et al., 2019a). However, the identification of a suitable low As accumulating rice variety and its use in breeding programs for the development of a suitable rice variety is also time consuming (Dave et al., 2013). To tackle the problem, the use of sustainable, feasible, and easily applicable agronomic management practices can be an effective strategy.

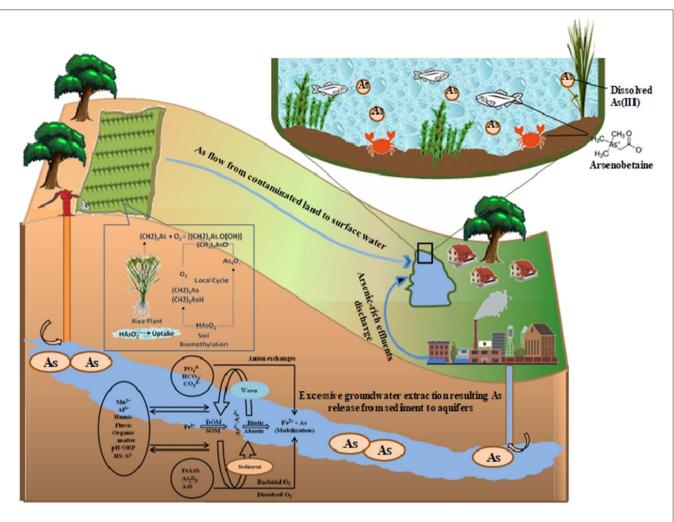
AGRONOMIC STRATEGIES FOR AS REDUCTION IN RICE

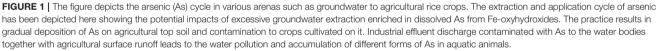
Various agronomic practices have been examined for reducing grain As concentration in rice plants. These include water management [alternate wetting-drying (AWD), aerobic sprinkler irrigation], nutrient management irrigation, (phosphate, nitrogen, iron, selenium, silica, etc.), biological approaches (microbial, algal, and fungal inoculation), soil inversion, biochar, and nanoparticle amendments, and so on (Li et al., 2009, 2019; Norton et al., 2009; Moreno-Jiménez et al., 2014; Chauhan et al., 2017; Yu et al., 2017; Awasthi et al., 2018; Huhmann et al., 2019; Seyfferth et al., 2019; Srivastava et al., 2019) (Table 1). Recently, Upadhyay et al. (2018) discussed about the feasible utilization of plant growth-promoting microorganisms for the amelioration of As toxicity in plants. A recently utilized practical approach of Huhmann et al. (2019) was to excavate soil in three layers (top 20 cm and two layers of 10 cm each) and to simply invert the soil with the lowermost layer placed on top and uppermost layer at bottom. This led to a reduction in soil As around the rice root zone and also resulted in a significant increase in rice yields. However, the sustainability of the approach was questioned by the authors themselves. The benefits of inversion would not last a few decades until the upper layers again become laden with As brought from As-containing groundwater (Huhmann et al., 2019). Similarly, there are pros and cons of other management approaches also and in each of these approaches; the water supply itself plays a role in regulating eventual As levels in rice grains. Because water being used for irrigation is laden with As in contaminated areas, it appears worthwhile to develop an agronomic strategy based on water management either solely or in combination with other appropriate strategies. The following discussion is focused on water management-based approaches targeted at As reduction in rice grains.

RICE-WATER INTERACTIONS: RADIAL OXYGEN LOSS AND IRON PLAQUE FORMATION

Groundwater used for irrigation is not only the source of As for rice fields but also an important regulator of As chemistry and bioavailability in rice fields. In the conventional method of rice irrigation, the fields are flooded throughout the growth period of rice plants (Shrivastava et al., 2019). Rice is a semiaquatic plant, and sufficient water availability plays a key role in achieving proper rice growth and productivity (Islam et al., 2019). The As cycle is a complex phenomenon and is influenced by various factors (**Figure 1**). Owing to continued water stagnancy in rice fields, anaerobic conditions are generated, and As release from the dissolution of Fe oxyhydroxides is promoted (Majumdar and Bose, 2018). As(III) tends to become attached to Fe oxides more TABLE 1 Different agronomic management approaches studied through which As accumulation in rice grains can be reduced.

| S. No. | Agronomic management approach | Amendment | Mode of application | Result/effect | Mechanism | References |
|--------|--|---|--|---|--|--|
| 1. | Nutrients management | Application of Si | Direct soil amendment in natural field conditions | 25–50% reduction in grain As level | Reduction in As uptake through increased fraction of ferrihydrite in root plaque; competition with As(III); <i>OsLsi1</i> downregulation | Seyfferth and Fendorf, 2012; Limmer et al., 2018 |
| | | Application of N | Hydroponic medium supplementation | 41% reduction in As content in 7 days old rice seedling root | Alteration of root architecture | Srivastava et al., 2019 |
| | | Application of S | Hydroponic medium supplementation | - | Improved thiol and antioxidant metabolism; Fe plaque formation | Zhang et al., 2011; Dixit et al., 2015 |
| | | Application of P | Direct soil amendment in natural As contaminated field in Bangladesh | 10% reduction of As in rice grain | Competition with As(V) during uptake; improvement in redox homeostasis | Talukder et al., 2011 |
| | | Application of Fe/Fe oxide | Direct soil amendment in natural field conditions | 51 and 47% As reduction in rice grain, respectively, by using iron and iron oxide | Immobilization of As owing to the formation of Fe plaque; reduction in oxidative stress, changes in expression of metallothionines | Nath et al., 2014; Farrow et al., 2015; Matsumoto et al., 2015 |
| 2. | Other technical agronomic inventions | Nanostructured α -MnO ₂ | Direct soil amendment in pot study | 17.8, 36.4, 65.4, and 60.7% As reduction in 0.2, 0.5, 1, and 2% $\alpha\text{-MnO}_2$ amendment, respectively | Bioavailability control (reduction) of As in soil and the associated influx of As into different rice tissues | Li et al., 2019 |
| | | Leonardite | Direct soil amendment in pot study | 31.6% reduction in rice grain by using 1% w/v Leonardite | Downregulation of OsLsi1, OsLsi2 and OsPT4 | Dolphen and Thiravetyan, 2019 |
| | | Application of biochar | Direct soil amendment in natural field conditions | 3, 6, and 14% As reduction in rice grain by using 0.5, 1, 2% manganese oxide–modified biochar | Formation of Fe plaque and reduced As(V) uptake | Yu et al., 2017 |
| | | Agricultural soil inversion strategy | Directly inversion of soil | 40% reduction in paddy soil As concentration by using this inversion technique | Presence of low As soil layer on top around rice roots | Huhmann et al., 2019 |
| 3. | Biological approaches | Application of microbes, algae and fungal inoculation (either individually or in as consortium) | Hydroponic medium supplementation; direct soil amendment in As spiked soil in pot study | 82.2 and 79.5% reduction in As accumulation in rice plant tissue by using AB402 and AB403 bacterial isolates; 52 and 47% reduction in As accumulation in root and shoot of rice tissue | Improved thiols (cysteine and NPTs) synthesis and enzyme activities (SAT and CS) involved in thiol metabolism | Awasthi et al., 2018; Mallick et al., 2018; |
| 4. | Selection of As safe rice cultivar | Naturally acclimatized to accumulate lesser amount of As in grain | Naturally existed | Varies from variety to variety and site to site | Reduced uptake of As from soil | Norton et al., 2009; Punshon et al., 2017 |
| 5. | Water management approaches | Alternate wetting–drying (AWD) | Change in irrigation regimen pattern | 61 and 68% reduction in rice grain in AWD35 and AWD25 (volumetric water content was 35 and 25%, respectively) treatment in 2015 field trial; 26% reduction in As content in rice grain | Increased soil aeration and lesser mobilization of inorganic As in soil | Norton et al., 2017; Carrijo et al., 2018 |
| | | Sprinkler irrigation | Change in irrigation regimen pattern | 63 and 83% reduction in rice grain As content in 1-year and 7-years field trials, respectively | Reduction in the methylation process and changes in rice grain As speciation | Moreno-Jiménez et al. 2014 |
| | | Intermittent flooding | Change in irrigation regimen pattern | From 40 to 63% reduction in As content gradually in consecutive years (2013–2016) | Enhanced Si bioavailability and reduced As bioavailability to the plant from soil | Majumdar et al., 2019; Shrivastava et al., 201 |
| | | Raised bed cultivation | Furrow cultivation | Yearly, 30% less As buildup in soil and further lesser accumulation in rice grain too | Lesser bioavailability of As in soil as it was mostly bound with Fe in soil owing to fewer redox changes | Duxbury and Panaullah, 2007; Talukder et al., 2011 |
| 6. | Pisciculture | Through "Rizi-pisciculture" | Maintenance of oxidized conditions in rice fields | Partially manage the As contamination along with 6–15% increment in rice total yield and growth | Lesser dissolution of As(V) from Fe–Mn complexes; greater aeration of the soil-aqueous system | Schuster, 1955; Coche, 1967; Majumdar et al., 2020 |





frequently than As(V) and its concomitant release by microbial reduction, alteration in pH and redox coupling, and changes in organic matter results in increased bioavailability of more soluble As(III) (Majumdar et al., 2019). Water management must be practiced in such a way so as to reduce As loading in rice grains without affecting rice yields. Rice plants release oxygen through their roots, and this leads to iron plaque formation on the root surface (Mei et al., 2012; Majumdar et al., 2020). Iron plaque can act as a major sink or source of As to rice plants (Tripathi et al., 2014). Hence, water management of rice fields can also modify As bioavailability to rice plants through changes in oxygen release from rice plants and subsequent iron plaque formation on rice roots.

REDUCED FLOODING/SEMIAEROBIC AND AEROBIC CULTIVATION

The practice of intermittent irrigation/semiaerobic irrigation has been found to result in optimum rice yields (Norton et al., 2017).

This involves the periodical application of water to moisten the rice field followed by a drying phase. The whole Southeast Asia is an agricultural rich belt including the Indian subcontinent, which depends on intensive agriculture and consumes large amounts of groundwater for irrigation purpose in rice paddy fields. The reduced flooding cultivation such as sprinkler irrigation or AWD not only would indeed save groundwater but would also increase the organic content in the soil, which is known to be a key driver to agricultural production. The cycle of drywet phases also allows lesser translocation of As from soil to rice plants (Carrijo et al., 2018). During the growth cycle of rice plants, inflorescence- and grain-filling stages are crucial because most of the As is translocated to the grains during these stages (Majumdar and Bose, 2018). Semiaerobic cultivation generates less reducing conditions during the dry phase, leading to decreases in As bioavailability to the plants (Moreno-Jiménez et al., 2014; Majumdar et al., 2020). The continuous application of the dry phase for longer time periods (aerobic cultivation) reduces the soil As bioavailability to a greater extent and also causes less As accumulation in rice grains. However, it decreases total yield and productivity. Aerobic cultivation has also been found to increase cadmium (Cd) content in rice grain (Yuan et al., 2019).

OTHER METHODS OF WATER MANAGEMENT

The other alternative methods of water application in rice cultivation include sprinkler irrigation (Table 1). Sprinkler irrigation can be used in fields to spread water from the top, keeping both the plants and soil moist without flooding the soil and hence reducing As loading to the rice grains (Majumdar et al., 2020). Moreno-Jiménez et al. (2014) tested the efficiency of sprinkler irrigation in reducing rice grain As. They found that sprinkler irrigation was able to reduce grain total As by one-third in only one application as compared to traditional irrigation. With continuous use of sprinkler irrigation, a significantly high reduction in grain total As was noticed in comparison to traditional irrigation. Further, the level of organic As was also lower in sprinkler irrigation. However, they did notice an increase in Cd concentration in rice grains as a consequence of sprinkler irrigation (Moreno-Jiménez et al., 2014). The reduction in mobility of soil As and reduction in the bioavailability of As to plants were noticed with the use of sprinkler irrigation by Spanu et al. (2012).

Another alternative is to simply avoid irrigation with groundwater and rely only on rain-fed rice cultivation. This is a simple and effective method. However, this would preclude summer season rice cultivation. Nevertheless, if proper rainwater storage could be achieved, and furrows were constructed for irrigation, rainwater-mediated irrigation could be practiced even during the summer season. In rainwater, presence of As is minimal. The application of rainwater in a furrow-like channel not only would provide necessary water to rice plants but also would avoid mobilization of soil As in high amounts as compared with conventional waterlogged cultivation (Sharma et al., 2014). During rain-fed irrigation in alkaline soils of paddy fields, the oxidative status of As and soil pH change and consequently the mobilization pattern of As are changed (Sultan and Dowling, 2006), leading to decreases in As accumulation in the top soil layer during the Aman season (monsoonal period) compared to Boro season (dry winter season) (Dittmar et al., 2010).

The stagnant water in the rice field resulting from flooded irrigation practices can also be used for the coculture of fishes. This is known as rizi-pisciculture. This method can also

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modulate the As concentration and its bioavailability in rice fields (Majumdar et al., 2020). The application of pisciculture has been established in China (Renkui et al., 1996), Thailand (Little et al., 1996), Vietnam (Berg, 2002), Bangladesh (Haroon and Pittman, 1997), and India (Das, 2002). Fish can also absorb As from the aqueous phase through their gills and convert it to less toxic organic forms such as arsenobetaine (Eisler, 1988; Majumdar et al., 2020). Therefore, the use of fish farming could be a sustainable solution to tackle As contamination in rice plants up to a certain extent.

In conclusion, As contamination of rice grains can be mitigated through effective water management strategies. This area needs more research and standardization to provide a sustainable option to reduce rice grain As for years to come. There is also a need to develop policies in this respect to restrict the use of highly As-contaminated bore wells and to lessen the extraction of excessive amounts of groundwater (Sekar and Randhir, 2009). This also entails that community-level participation is necessary to manage the As problem sustainably. The study conducted by Upadhyay et al. (2019b) in two remote villages of West Bengal demonstrated the yet prevalent lack of awareness among people and suggested the need for providing basic knowledge to tackle the As problem. Additionally, attention and coordination between stakeholders and government bodies are crucial to tackle the problem (Bhatia et al., 2014). There is also a need to integrate various potential agronomic practices in future research to achieve the desirable reduction in rice grain As.

AUTHOR CONTRIBUTIONS

SS conceptualized the manuscript background and also revised and wrote the manuscript. MU and AM wrote the manuscript, prepared Table. JS partial write up and Figure preparation. Lastly, all the authors approves the manuscript.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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